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TG/DTA STUDIES ON GAMMA-IRRADIATED AMMONIUM PERCHLORATE AND ITS MIXTURES WITH KCl/KBr

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While normal ammonium perchlorate (AP) decomposes in two stages (at 315 and 375 °C), its 20% weight loss occurred even at 160 °C when it had absorbed 1.0 MGy dose. Increased crystal size caused further changes in the TG/DTA curves. Characteristics: the above weight loss approached 85% for 20 times larger particles. AP mixed with KCl/KBr in 1 : 1 ratio showed formation of potassium perchlorate on heating and the quantity increased progressively when the AP was pre-treated by irradiation.

The decomposition of ammonium perchlorate (AP) has been studied widely using different thermal analysis [1–4] techniques. Normally there is an endothermic change at about 240° due to the orthorhombic →cubic phase transition, while above 300° two exotherms appear which correspond to decomposition. Kinetic data on isothermal heating demonstrated [5] the enhancement of the rate as well as the extent of AP decomposition when it was treated by gamma radiation. Our earlier IR spectral studies [6] on irradiated AP made in situ while heating was continued, showed a faster loss of all the peak intensities as compared to the untreated sample. Since potassium halide was used as a matrix during the IR investigations, it was of interest to know the thermal properties of gamma treated AP and particularly when AP was mixed with KBr/KCl.

Experimental

Commercial grade AP was collected in different particle sizes after its recrystallization. Physical mixtures of AP + KCl/KBr were prepared using particles of size 5×10^{-2} mm. Gamma irradiation was effected at a dose rate of 4.5 kGy h^{-1}

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using a ^{60}CO source. A Netzsch STA–409 thermal analyzer was employed for the thermal analysis; heating of a 20 mg sample was carried out at the rate of 10 deg min^{-1}.

Results and discussion

The data on normal and gamma irradiated AP presented in Fig. 1 show that the usual orthorhombic →cubic phase transformation endotherm remains at 243° even after the absorption of 1 MGy dose. The AP particles were of a size less than 0.05 mm. While there is a two stage exothermic weight loss for normal AP, namely, 30% at 315° and the remaining 70% at 375°, the pattern changed considerably for the radiolysed sample; as the dose was increased a new step developed over the lower temperature range prior to the endotherm and without affecting the DTA trend. At 0.5 MGy dose a 10% weight loss occurred at 240° and when the dose was increased to 1.0 MGy, the temperature further lowered reaching 160° and yielding around 20% loss. Again, the loss was found to be dependent on the crystal size as well, increasing to the extent of 85% when the particle size of the irradiated sample was increased to 1 mm. It is to be noted that non-irradiated samples practically showed the same TG pattern when the particle size was varied from 0.05 to 1 mm.

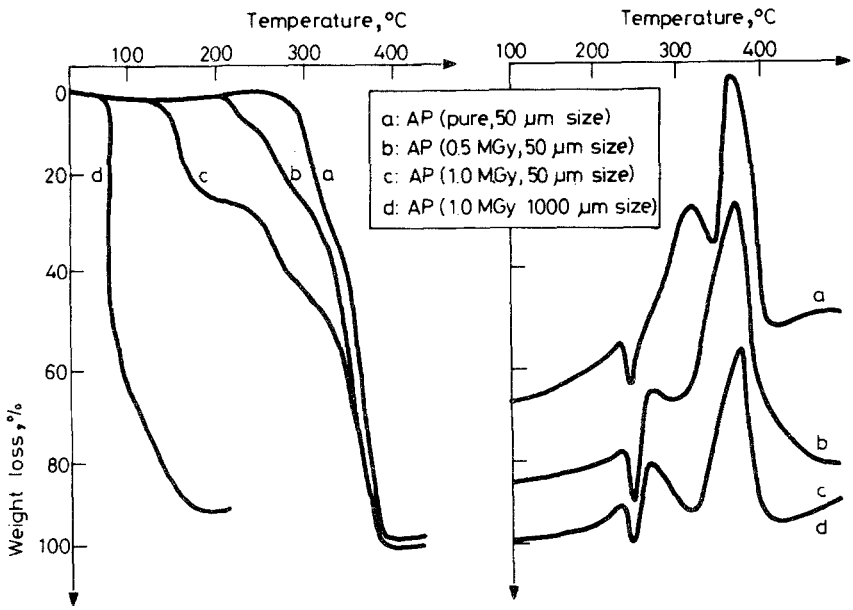

Fig. 1 Radiation effects on the thermal decomposition characteristics of AP

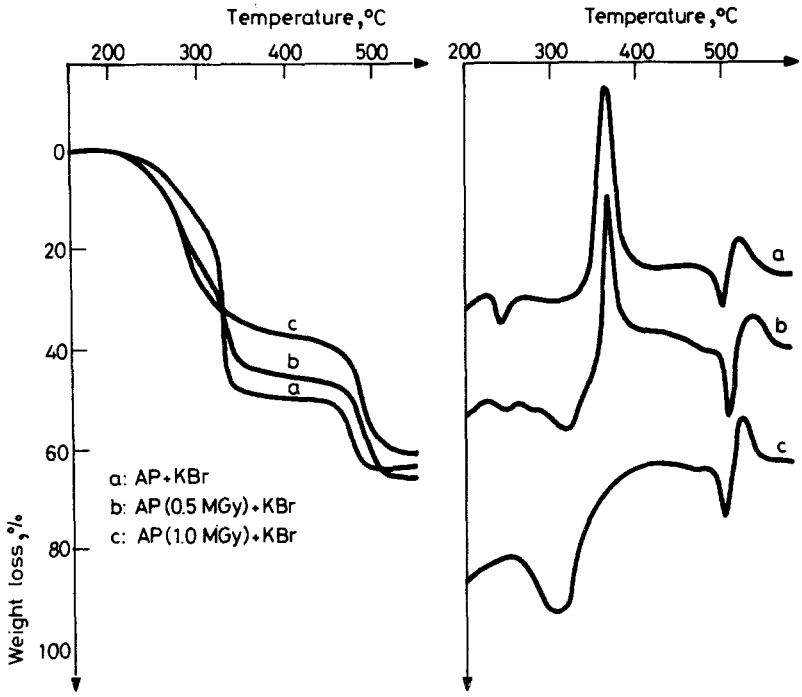

Fig. 2 Thermal characteristics of AP+KBr mixture (1 : 1 weight ratio)

Since most of the irradiated AP with larger particle size decomposes at 160°, the exotherms at higher temperatures vanish. But for the lower particle size the DTA data revealed that the temperature of the first exotherm is lowered by radiation, with the second exotherm remaining unaffected.

It is well known [7] that even 2% by weight of certain additives are effective in suppressing the first exotherm. The data obtained from thermogravimetric and differential thermal analyses for non-irradiated and irradiated AP mixed with KBr are given in Fig. 2. It is seen that the weight loss here is occurring in three stages: the first one (~320°) is endothermic and appears when the usual phase transition temperature is over; the second and the third stages are exothermic (375 and 525°). Thus in the presence of the halide matrix there is a total suppression of the characteristic first exotherm that normally appears at 315°, while the positions of the second deflagration exotherm and the phase transition endotherm remained unaltered. As the dose is increased the weight loss over the first and the third stages increases while that over the second stage decreases (see Table 1). Using Horowitz and Metzger's [8] relation the activation energies involved in the second and third stages were calculated. The value over the second stage for non-irradiated AP in its mixture with KBr is 166 kJ mol^{-1} which matches with the known value for pure AP decomposition. The activation energy observed over the third stage is

Table 1 Weight loss of AP mixed with KBr or KCl (wt. ratio 1 : 1) over different stages

Samples	Weight loss, %		
	Stage 1	Stage 2	Stage 3
AP + KBr	15	35	13
AP (0.5 MGy) + KBr	21	22	18
AP (1.0 MGy) + KBr	30	10	20
AP + KCl	9	25	15
AP (0.5 MGy) + KCl	22	—	21
AP (1.0 MGy) + KCl	27	—	26

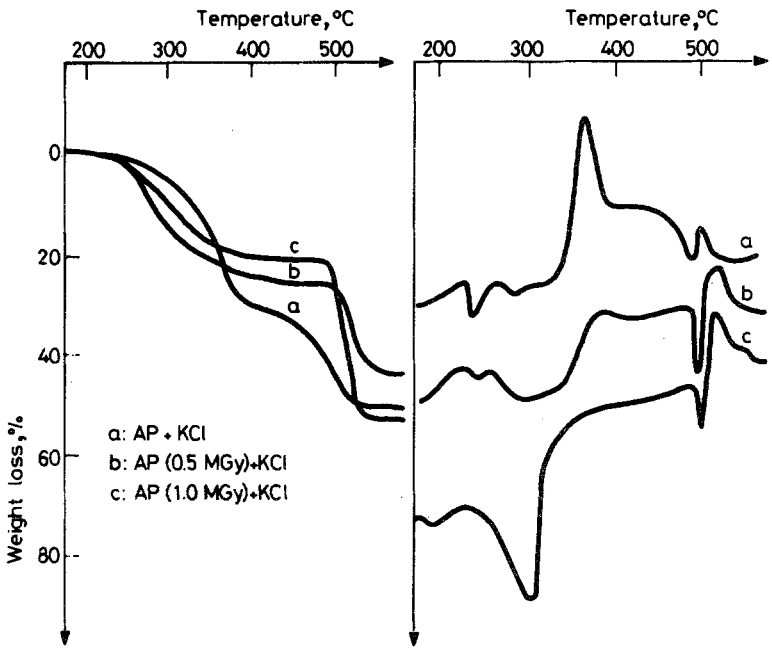

Fig. 3 Thermal characteristics of AP + KCl mixture (1 : 1 weight ratio)

176 kJ mol^{-1} which may be ascribed to the decomposition of $KClO_4$ which is likely to be formed [9] during the decomposition of AP in the presence of KBr. The TG/DTA data for AP + KCl mixtures (Fig. 3) are similar to those obtained for the AP + KBr mixtures; the difference lies in that the loss over the first and third stages is greater and over the second stage smaller in the former case.

The low-temperature loss may be attributed to the desorption of trapped gases, produced while AP irradiation is going on. Interestingly, however, the heat change

involved in the desorption remains undetected by the DTA curve. This process seems to be much more effective when the size of the crystal is increased. Furthermore when AP was irradiated the first exotherm that corresponds to a partial decomposition at 314° shifts to still lower temperature and with additional decomposition. This increased radiation-induced reactivity in part is probably due to the formation of positive holes which promote the electron-transfer process. The radiolytically formed [10] chlorate

$$ClO_4^- \rightarrow ClO_3^- + O \quad (1)$$

$$ClO_4^- + O \rightarrow ClO_3^- + O_2 \quad (2)$$

ions are also known to be effective accelerators [11] of AP decomposition. The observation that there is no shift in the second exotherm (375°) indicates that the above processes are operative only in the lower temperature range.

The endothermic weight loss of powder mixtures of AP+KBr and AP+KCl over the temperature range of 285–320° suggests the existence of a new compound. The following reaction is envisaged.

$$NH_4ClO_4 + KX \rightarrow NH_4X + KClO_4 \quad (3)$$

where the ammonium halide escapes from the lattice and the relatively stable compound $KClO_4$ is formed. The TG/DTA characteristics of the residue suggest that it contains $KClO_4$ together with a small fraction of partially untreated AP. The expected loss in weight due to the escape of NH_4Cl is 27% while the observed loss is only 9%. This means that a fraction of AP remains intact at the observed exotherm at 375°. The data further indicate that the reaction normally taking place to partial completion around 320°, goes to completion because of gamma irradiation. In the case of KBr matrix the expected loss in weight due to the escape of NH_4Br is 41.4% while the observed loss is only 15%. As has been expected the endothermic weight loss due to reaction (1) is increased due to the radiation treatment; however, unlike in KCl matrix the weight loss does not reach the optimum value after the absorption of 1 MGy dose. Reaction (1) is facilitated because of the ionization effect if AP is irradiated. The radiolyzed products like ClO_3, ClO_2, Cl_2 etc., are likely to escape during heating along with NH_4X. A just detectable hump at the position of the exothermic decomposition position indicated that a very small fraction of AP remained in the pure form escaping even after the irradiation.

Over the range of high temperatures between 500 and 600°, the potassium perchlorate quantitatively decomposes in both matrices following the reaction

$$KClO_4 \rightarrow KCl + 2O_2 \quad (4)$$

giving potassium chloride as a residue. The calculated weight loss due to the overall reaction is 50–55% while the observed value is about 7–10% higher. This difference can be accounted for if a loss of some KCl itself is presumed during the overall process.

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Zusammenfassung — Während sich normales Ammoniumperchlorat (AP) in zwei Schritten zersetzt (bei 315 und 375 °C), tritt nach vorher absorbierter Dosis von 1.0 MGy ein 20%-iger Massenverlust schon bei 160 °C auf. Eine erhöhte Kristallgröße verursacht weitere Veränderungen an TG- und DTA-Kurven: bei 20 mal größeren Partikeln erreicht der obengenannte Massenverlust 85%. Nach Vermischen von AP mit KCl/KBr im Verhältnis 1 : 1 wird bei Erhitzen Kaliumperchlorat gebildet, wobei die Ausbeute nach einer Vorbehandlung des AP durch Bestrahlung progressiv anwächst.

Резюме — В то время как чистый перхлорат аммония разлагается в две стадии при температуре 315 и 375° С, поглощенная им доза облучения равная 1,0 MGy приводит к 20% потере веса уже при температуре 160 °С. Увеличение размеров кристаллов вызывает дальнейшее изменение кривыс ТГ/ДТА. Вышеуказанная потеря веса приближается к 85% в случае кристаллов с 20 разовым увеличением. Перхлорат аммония, смешанный с хлорид-бромидом калия в соотношении 1 : 1, показал образование при нагревании перхлората калия, количество которого увеличивалось при предварительном облучении перхлората аммония.